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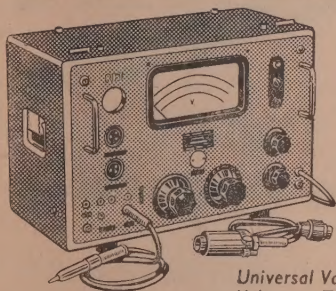   - Half page .. .. Rs. 30/- per insertion
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DETERMINATION OF THE ELASTIC CONSTANTS OF TETRAGONAL (4, 4, 4/m) CRYSTALS FROM THE STUDY OF DIFFUSE X-RAY REFLECTIONS

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ABSTRACT. Theoretical relationships connecting diffusely scattered X-ray inten-
sities from crystals with its elastic constants have been derived for tetragonal crystals of classes
4, 4 and 4/m. Methods of evaluation of all the seven elastic constants for these types of crystals
from a quantitative measurement of diffuse X-ray scattering only, have been described and
the results are being used to determine elastic constants of single crystals of Penta-erythritol
(Tetragonal 4).

The elastic properties of tetragonal crystals belonging to the point groups
4, $\overline{4}$, 4/m are defined by the matrix (according to the classical theory of elasticity)

$$
\begin{matrix}
C_{11} & C_{12} & C_{13} & 0 & 0 & C_{16} \\
 & C_{11} & C_{13} & 0 & 0 & -C_{16} \\
 & & C_{33} & 0 & 0 & 0 \\
 & & & C_{44} & 0 & 0 \\
 & & & & C_{44} & 0 \\
 & & & & & C_{66}
\end{matrix}
$$

where C_{11}, etc. are the elastic constants of the crystal.

The relations for the evaluation of the elastic constants of the tetragonal
crystals of more symmetrical point groups (namely, 42, $\overline{4}$2m, 4/mmm) from the
intensity measurement of thermal diffuse scattering of X-rays, have been derived
by Prasad and Wooster (1955). The intensity of diffuse X-ray scattering (1st
order only) from a small element of volume of the crystal along a line passing
through a reciprocal lattice point (*hkl*) which is responsible for the diffuse scatter-
ing, is proportional to the value of the expression $K[uvw]_{hkl}$ (designated as rekha
constant by Ramchandran and Wooster, 1951)
where,

$$
K[uvw]_{hkl} = L^2 A^{-1}{}_{11} + M^2 A^{-1}{}_{22} + N^2 A^{-1}{}_{33} + 2MN A^{-1}{}_{23} + 2NL A^{-1}{}_{31} + 2LM A^{-1}{}_{22}
$$

where L, M, N, are the direction cosines of the reciprocal lattice vector with respect to the crystal axes (the elastic axes also coincide with the crystal axes for these cases) and u, v, w are the direction cosines of the thermal wave vector and A^{-1}_{11} etc. are the elements of the matrix inverse to the matrix A_{ij} whose elements for tetragonal crystals of classes. 42, $\bar{4}$2m 4mm and 4/mmm are given by

$$A_{11} = C_{11}u^2 + C_{66}v^2 + C_{44}w^2$$
$$A_{22} = C_{66}u^2 + C_{11}v^2 + C_{44}w^2$$
$$A_{33} = C_{44}(u^2 + v^2) + C_{33}w^2$$
$$A_{23} = vw(C_{44} + C_{13})$$
$$A_{31} = wu(C_{44} + C_{13})$$
$$A_{12} = vu(C_{66} + C_{12})$$

Prasad and Wooster have also indicated that for very simple and elementary directions of the reciprocal lattice vector and the thermal wave vector, the values of K [u, v, w]$_{hkl}$ depend on one or two elestic constants only. Consequently, in principle, all the elastic constants can be evaluated without difficulty from the measurements of the intensities of the diffusely scattered X-rays along these directions. Since $C_{16} = -C_{26} \neq 0$ for the crystal classes which have been dealt with in this paper (whereas $C_{16} = C_{26} = 0$ for the classes considered by Prasad and Wooster) the values of $K[uvw]_{hkl}$ involve many elastic constants even for simple reciprocal lattice vectors and simple directions of thermal wave vectors. Hence determination of all the elastic constants from X-ray measurements is apparently quite difficult, as will be evident from the succeeding text where the relationships and the method to be applied in such cases have been described. It can be shown that the elements of the matrix A_{ij} for tetragonal crystals of classes 4, $\bar{4}$, and 4/m are given by :

$$A_{11} = C_{11}u^2 + C_{66}v^2 + C_{44}w^2 + 2uvC_{16}$$
$$A_{22} = C_{66}u^2 + C_{11}v^2 + C_{44}w^2 - 2uvC_{16}$$
$$A_{33} = C_{44}(u^2 + v^2) + C_{33}w^2$$
$$A_{23} = vw(C_{44} + C_{13})$$
$$A_{31} = wu(C_{44} + C_{13})$$
$$A_{12} = (u^2 - v^2)C_{16} + uv(C_{66} + C_{12})$$

Values of the $K[uvw]_{hkl}$ derived for the present cases for some reciprocal lattice points and some simple directions of propagation of the thermal waves are given in Table I.

It can be seen from Table I that the constants C_{44} and C_{33} can be determined independently from observations along [001]$_{\bar{h}oo}$ and [001]$_{ool}$ yielding the values

TABLE I.

K values for the tetragonal crystal classes (4, $\bar{4}$ and $4/m$)

Direction cosines $(u,v,w,)$ of the direction of progration of the thermal wave.	Index of the reciprocal lattice points			
	hoo	hko	ool	hol
100	$\left[C_{66}/(C_{11}C_{66}-C_{16}^2) \right]$	$\left[\dfrac{L^2C_{66}+M^2C_{11}-2LMC_{16}}{(C_{11}C_{66}-C_{16}^2)} \right]$	$1/C_{44}$	$\left[L^2C_{66}/(C_{11}C_{66}-C_{16}^2)+N^2/C_{44} \right]$
010	$\left[C_{11}/(C_{11}C_{66}-C_{16}^2) \right]$	$\left[\dfrac{L^2C_{11}+M^2C_{66}+2LMC_{16}}{(C_{11}C_{66}-C_{16}^2)} \right]$	$1/C_{44}$	$\left[L^2C_{11}/(C_{11}C_{66}-C_{16}^2)+N^2/C_{44} \right]$
001	$1/C_{44}$	$(L^2+M^2)/C_{44}$	$1/C_{33}$	$\left[L^2/C_{44}+N^2/C_{33} \right]$
$\left(\dfrac{1}{\sqrt2},0,\dfrac{1}{\sqrt2}\right)$	$\dfrac{2[(C_{66}+C_{44})(C_{44}+C_{33})]}{\Delta}$		$\dfrac{2[(C_{66}+C_{44})(C_{44}+C_{11})-C_{16}^2]}{\Delta}$	$L^2K\left[\dfrac{1}{\sqrt2}\ 0\ \dfrac{1}{\sqrt2}\right]_{hoo}$ $+\,N^2K\left[\dfrac{1}{\sqrt2},0,\dfrac{1}{\sqrt2}\right]_{ool}$ $+\,\dfrac{4NL(C_{44}+C_{33})(C_{44}+C_{33})}{\Delta}$
$\left(-\dfrac{1}{\sqrt2},0,\dfrac{1}{\sqrt2}\right)$ or $\left(\dfrac{1}{\sqrt2},0,-\dfrac{1}{\sqrt2}\right)$	,,		,,	$L^2K\left[\dfrac{1}{\sqrt2}\ 0\ \dfrac{1}{\sqrt2}\right]_{hoo}$ $+\,N^2K\left[\dfrac{1}{\sqrt2},0,\dfrac{1}{\sqrt2}\right]_{ool}$ $-\,\dfrac{4NL(C_{44}+C_{33})(C_{44}+C_{33})}{\Delta}$

where $\Delta = [(C_{44}+C_{11})(C_{66}+C_{44})(C_{44}+C_{33}) - C_{16}^2(C_{44}+C_{33}) - (C_{44}+C_{13})^2(C_{66}+C_{44})]$

TABLE I (contd.)

K values for the tetragonal crystal classes (4, 4̄ and 4/m)

Direction cosines (u,v,w) of the direction of propagation of the thermal wave.	Index of the reciprocal lattice points			
	hoo	ool	hko	hol
$\left(\dfrac{1}{\sqrt{2}},\ \dfrac{1}{\sqrt{2}},\ 0\right)$	$\left[\dfrac{2(C_{66}+C_{11}}{C_{11}^2+2C_{66}}\quad\dfrac{-2C_{16}}{(C_{11}-C_{12})-C_{12}^2-4C_{16}^2}\right]$	$1/C_{44}$		
$\left(\dfrac{1}{\sqrt{2}},\ \dfrac{1}{\sqrt{2}}\right)$ or $\left(\dfrac{1}{\sqrt{2}},\ -\dfrac{1}{\sqrt{2}},\ 0\right)$	$\left[\dfrac{2(C_{66}+C_{11}}{C_{11}^2+2C_{66}}\quad\dfrac{-2C_{16}}{(C_{11}-C_{12})-C_{12}^2-4C_{16}^2}\right]$	$1/C_{44}$		
$\left(0,\ \dfrac{1}{\sqrt{2}},\ \dfrac{1}{\sqrt{2}}\right)$ or $\left(0,\ -\dfrac{1}{\sqrt{2}},\ \dfrac{1}{\sqrt{2}}\right)$ or $\left(0,\ \dfrac{1}{\sqrt{2}},\ -\dfrac{1}{\sqrt{2}}\right)$	$\dfrac{2[(C_{44}+C_{33})(C_{11}+C_{44})-(C_{44}+C_{13})^2]}{\Delta}$	$\dfrac{2[(C_{66}+C_{44})(C_{11}+C_{44})-C_{16}^2]}{\Delta}$		

where $\Delta = [(C_{44}+C_{11})(C_{66}+C_{44})(C_{44}+C_{33})-C_{16}^2(C_{44}+C_{33})-(C_{44}+C_{13})^2(C_{66}+C_{44})]$

of $K[001]_{hoo}$ and $K[001]_{ool}$ respectively. The value of C_{44} can also be evaluated
from observations along [001] for different (hko) reciprocal lattice nodes and also
from $K(010)_{001}$. Further, the values of C_{44} and C_{33} can be simultaneously obtained
from observations along [001] for at least two different (hol) reciprocal lattice
nodes. Since such determined values of C_{44} and C_{33} are dependent on two observed
K-values, its accuracy of determination is theoretically less than that mentioned
at the beginning. Again, by substituting the value of C_{44} in the observed value
of $K[001]$, the value of C_{33} can be determined easily considering one (hol) reci-
procal lattice node only at a time. To increase the accuracy of thus determined
value of C_{33}, we are to choose a reciprocal lattice node for which the value of L
is very low compared to that of N, i.e. a node whose l index is much higher than
its h index; in such condition the value of $K[001]_{hol} = [L^2/C_{44} + N^2 C_{33}]$ will be
guided primarily by the value of N^2/C_{33}. The value of C_{44} can further be deter-
mined by combining the observed value of $K[100]_{hol}$ with $K[100]_{hoo}$ and $K[010]_{hol}$
with $K[010]_{hoo}$. Alternatively, by substituting the value of C_{44} in $K[100]_{hol}$
and $K[010]_{hol}$, the values of $\dfrac{C_{66}}{(C_{11}C_{66} - C_{16}^2)}$ and $\dfrac{C_{11}}{(C_{11}C_{66} - C_{16}^3)}$ can be obtained
respectively from which we can get the ratio C_{11}/C_{66}. It will be seen further
that solution of more than one relation only gives the values of the ratio of the
constants (viz. C_{11}/C_{66}, etc.) and C_{11}, C_{66} and C_{16} cannot be determined indepen-
dently and directly. For determining the absolute values of these three constants,
the method of successive approximation suggested is as follows :

From the Table I, we have

$$\frac{1}{K[100]_{hoo}} = \left(C_{11} - \frac{C_{16}^2}{C_{66}} \right) \qquad \ldots \ (1)$$

$$\frac{1}{K[010]_{hoo}} = \left(C_{66} - \frac{C_{16}^2}{C_{11}} \right) \qquad \ldots \ (2)$$

and

$$K[100]_{hko} = \frac{(L^2 C_{66} + M^2 C_{11} - 2ML C_{16})}{C_{11}/K[010]} \qquad (3)$$

Substituting the experimentally determined values of $1/K[100]_{hoo}$ and
$1/K[010]_{hoo}$ for C_{11} and C_{66} respectively in the relation (3), we can thus get some
value for C_{16}. Let us now substitute in relation (1) this value of C_{16} along with
the experimentally determined value of $1/K[010]$ for C_{66}. We thus get some value
for C_{11}. These values of C_{11} and C_{16} may be substituted in the relation (2) to give
a better value for C_{66}. These values of C_{11} and C_{66} can now be substituted in
relation (3) to yield a better value for C_{16}. This value for C_{16} and C_{66} on substi-
tution in relation (1) gives a better value for C_{11} and so on. We can in this way go
on repeating the process again and again till further refinements do not change

the values of C_{11}, C_{66} and C_{16}. The smaller the value of C_{16} as compared to C_{11} and C_{66}, the lesser would be the number of repetitions needed. It should be re-remarked that this method of successive approximation does not assume anything regardingt he relative values of the constants involved. Actually a numerical example assuming tentatively $C_{11} = 2C_{66} = 4C_{16}$ required about four repetitions whereas in another example in which $C_{11} = 2C_{66} = 2C_{16}$, about eight repetitions were found to suffice. In fact the constant C_{16} relates an external stress to shear strain, therefore it would be expected for most of the cases to be smaller than the constants C_{44}, C_{55}, C_{66} which relate a shear stress to a shear strain in the same plane and considerably smaller than the constants C_{11}, C_{22}, C_{33} which relate an extentional stress to a collinear extentional strain. So in general not many repetitions will be required for getting the correct value of C_{11}, C_{66}, and C_{16}. Since we are to use three observational intensities each of which depends on these constants namely, C_{11}, C_{66} and C_{16} the values of C_{11}, C_{66}, C_{16} will be theoretically less accurate than the values of the constants C_{44} and C_{33} which have been derived from intensities depending on one constant only. But in practical cases, the determination of a particular elastic constant derived by using different value of $K[u, v, w]_{hkl}$, $K[u', v', w']_{h'k'l'}$ does not appreciably reduce the accuracy of its determination. Once we obtain the absolute values of the constants C_{11} and C_{66} by substituting the value of C_{11} in the ratio C_{11}/C_{66} which is obtained from different sources (as mentioned earlier), the value of C_{66} can be determined or vice versa. The constant C_{16} with proper sign can also be evaluated from the observed value of

$$\frac{K\left[\dfrac{1}{\sqrt{2}}, -\dfrac{1}{\sqrt{2}}, 0\right]_{h00}}{K\left[-\dfrac{1}{\sqrt{2}}, \dfrac{1}{\sqrt{2}}, 0\right]_{h00} \text{ or } K\left[\dfrac{1}{\sqrt{2}}, -\dfrac{1}{\sqrt{2}}, 0\right]_{h00}} = \frac{(C_{11}+C_{66}-2C_{16})}{(C_{11}+C_{66}+2C_{16})}$$

when the values of C_{11} and C_{66} are substituted there. Similarly from observations

$$\left[\frac{K\left[\dfrac{1}{\sqrt{2}}, 0, \dfrac{1}{\sqrt{2}}\right]_{h0l}}{K\left[-\dfrac{1}{\sqrt{2}}, 0, \dfrac{1}{\sqrt{2}}\right]_{h0l} \text{ or } K\left[\dfrac{1}{\sqrt{2}}, 0, -\dfrac{1}{\sqrt{2}}\right]_{h0l}}\right]$$

one obtains the value of the ratio

$$\frac{L^2[(C_{66}+C_{44})(C_{44}+C_{33})]+N^2[(C_{55}+C_{44})(C_{44}+C_{11})-C_{16}^2]+2LN(C_{44}+C_{33})(C_{33}+C_{13})}{L^2[(C_{66}+C_{44})(C_{44}+C_{33})]+N^2[(C_{66}+C_{44})(C_{44}+C_{11})-C_{16}^2]-2LN(C_{44}+C_{33})(C_{33}+C_{13})}$$

which, when the values of C_{11}, C_{33}, C_{44}, C_{66} and C_{16} are substituted, gives the value of C_{13} with proper sign. Again, if we substitute the values of C_{11}, C_{33}, C_{66}

and C_{16} in the observed values of $K\left[\dfrac{1}{\sqrt{2}}, 0, \dfrac{1}{\sqrt{2}}\right]_{hoo}$, $K\left[\dfrac{1}{\sqrt{2}}, 0, \dfrac{1}{\sqrt{2}}\right]_{ool}$

$K\left[0, \dfrac{1}{\sqrt{2}}, \dfrac{1}{\sqrt{2}}\right]_{hoo}$ and $K\left[0, -\dfrac{1}{\sqrt{2}}, \dfrac{1}{\sqrt{2}}\right]_{ool}$ each of which gives a second

degree equation in C_{13} and retain only the positive value of the solution under the surd, the value of the constant C_{13} can be evaluated with proper sign. The remaining constant C_{12} can be determined from the observed values of $K\left[\dfrac{1}{\sqrt{2}}, \dfrac{1}{\sqrt{2}}, 0\right]_{hoo}$

and $K\left[\dfrac{1}{\sqrt{2}}, 0, -\dfrac{1}{\sqrt{2}}\right]_{hoo}$ or $K\left[-\dfrac{1}{\sqrt{2}}, 0, \dfrac{1}{\sqrt{2}}\right]_{hoo}$ each of which gives a

second degree equation in C_{12} on substitution of the values of C_{11}, C_{66} and C_{16}; retaining only the positive values of the solution under the surd C_{12} with proper sign can be evaluated. Other more complex directions of observations can be taken for which K values depend on C_{12} in combination with the other constants and C_{12} can be evaluated from those expressions just proceeding in the same manner as before.

The relations derived and the method of evaluation of the elastic constants indicated above are being used for the determination of the seven elastic constants (C_{11}, C_{33}, C_{44}, C_{66}, C_{12}, C_{13} and C_{16}) of crystals of Pentaerythritol (Point Group 4) using the photographic method as developed by Chakraborty and Sen (1958) and the complete experimental results will be published in near future.

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SPLITTING OF NEUTRON ENERGY LEVELS DUE TO SPIN-ORBIT COUPLING

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CALCUTTA–32

ABSTRACT. Due to the spin-orbit interaction the splitting of the energy levels of neutrons moving in the potential $V = V(r) + \alpha \dfrac{\hbar^2}{M^2 C^2} \dfrac{1}{r} \dfrac{dV}{dr} \vec{\sigma}.\vec{l}$ is calculated for p-states for atomic mass 200. The effect of the spin-orbit coupling is calculated by the perturbation method with the unperturbed wave functions as obtained by Ghosh and Sil (in course of publication) by the technique of Lanczos.

For the calculation of energy levels of neutrons moving in the nucleus we choose the nuclear potential as of the form

$$V = V(r) + \alpha \frac{\hbar^2}{M^2 C^2} \frac{1}{r} \frac{dV}{dr} \vec{\sigma}.\vec{l}$$

where $\qquad V(r) = -V_0[1 + e^{(r-R)/a}]^{-1}$ and $\alpha = -\dfrac{15}{2}$

The constant α is the same as taken by Fermi (1954) for polarization of high energy protons scattered by nuclei. The operator $\vec{\sigma}.\vec{l}$ in the above expression can be replaced by its eigen values (cf. Mayer and Jensen, 1955). Thus

$$V = V(r) + \alpha \frac{\hbar^2}{M^2 C^2} \frac{1}{r} \frac{dV}{dr} l \qquad \text{for } j = l + \tfrac{1}{2}$$

$$= V(r) - \alpha \frac{\hbar^2}{M^2 C^2} \frac{1}{r} \frac{dV}{dr} (l+1) \qquad j = l - \tfrac{1}{2}$$

We shall consider the splitting of the energy levels due to the spin-orbit coupling term by the usual perturbation method; to obtain the unperturbed solutions, we neglect this term in the Schrodinger equation and solve it by a method due to Lanczos (1934). This procedure is previously (Chosh and Sil, 1960) adopted in obtaining the single particle bound states of neutrons moving in the

potential $V(r) = -V_0[1+e^{(r-R)/a}]^{-1}$. The separation of the perturbed state from the unperturbed level is given by

$$\Delta E = \int \psi^* H \psi d\tau$$

when H represents the perturbation and ψ is the unperturbed wave function (normalized).

Since the operator $\overrightarrow{\sigma} . \overrightarrow{l}$ in the perturbation has been replaced by its eigen values we need consider only the radial part of the integral. The range of the above integration is split up into four regions which are as follows : $I. 0 < r \leqslant r_1 = R-a \log_e 9$, $II\ r_1 \leqslant r \leqslant R$, $III.\ R \leqslant r \leqslant r_2 = R+a \log_e 9$ and $IV.\ r_2 \leqslant r < \infty$. The limits of r_1 and r_2 are so chosen that the nuclear potential drops respectively to 9/10 and 1/10 of its value at $r = 0$.

The unperturbed wave functions of the neutron in the four regions are :

$$\psi_I = j_l(\gamma x)$$

$$\psi_{II} = \frac{1}{x} [Ae^{i\gamma'x}\ F^+(q) + A^* e^{-i\gamma'x}\ F^-(q)]$$

$$\psi_{III} = \frac{1}{x} [A^+ e^{+k'x}\ F^+(p) + A^- e^{-k'x} F^-(p)]$$

and $\qquad \psi_{IV} = C h_l^{(1)}(ikx)$

where j_l and h_l are respectively the spherical Bessel and Hankel function of order l; F's are polynomials in p or q, further

$$p = \frac{1}{8}(9e^{(R-r)/a} - 1)$$

$$q = \frac{1}{8}(9e^{(r-R)/a} - 1)$$

$$\gamma = \sqrt{\lambda^2 - k^2}\ ; \qquad \gamma' = \sqrt{\lambda^2 - k''^2}$$

where $\qquad \lambda^2 = \frac{2M}{\hbar^2} V_0 a^2\ ; \quad k^2 = \frac{2M}{\hbar^2}\ |E| a^2$

$$k'^2 = k^2 + \frac{l(l+1)}{2} a^2 \left[\left(\frac{1}{R}\right)^2 + \left(\frac{1}{R+a \log_e 9}\right)^2\right]$$

$$k''^2 = k^2 + \frac{l(l+1)}{2} a^2 \left[\left(\frac{1}{R}\right)^2 + \left(\frac{1}{R-a \log_e 9}\right)^2\right]$$

2

The constants A, A^*, A', A^- and C of the unperturbed wave functions are determined by the usual matching of ψ_I, ψ_{II} and their derivatives at $r = r_1$, ψ_{II}, ψ_{IV} and their derivatives at $r = r_2$ and finally ψ_{II}, ψ_{III} and their derivatives at $r = R$. Since the spin-orbit interaction is only a surface effect, in this paper we have evaluated the perturbation integral only in the two short ranges r_1 to R and R to r_2 near the boundary. In these two short ranges we have evaluated the integral numerically applying Simpson's rule.

The parameters in the central part of the potential are $V_0 = 52$ Mev, $R = (1.15A^{1/3}+0.4)10^{-13}$cm, $a = 0.57 \times 10^{-13}$ cm. The calculated values of the separation of the levels for $j = 1/2$ and $j = 3/2$ for atomic mass 200 are shown in Table I.

TABLE I

State	Separation between the states $j = 1/2$ and $j = 3/2$
$1p$	0.69 MeV
$2p$	0.70 MeV
$3p$	0.83 MeV

In conclusion we may mention that for atomic mass 208 Ross *et al.* (1956) have obtained a separation of nearly 0.9 Mev. between $3p_{\frac{1}{2}}$ and $3p_{3/2}$ states. In our case for $A = 200$ we have obtained a separation of 0.8 MeV.

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SPACE GROUPS OF CRYSTALS OF ORTHO, META AND PARAXYLENE AT −180°C*

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Plate IV

ABSTRACT. The Debye-Scherrer patterns of o-xylene, m-xylene and p-xylene frozen and cooled to −180°C have been photographed and analysed. The analysis has given the unit cell dimensions which explain all the reflections. The densities of the substances have been determined and have been found to be 1.032, 1.030 and 1.006 gm cm^{-3} respectively for the ortho-, meta- and para compound. From these data the space group has been found in each case. The crystals of o-xylene belong to the orthorhombic system with $a = 8.77$, $b = 10.20$ and $c = 14.55$ Å. The number of molecules per unit cell is 8 and the space group is $Pmmm$. The crystals of m-xylene also belong to the orthorhombic system. The dimensions of the unit cell are : $a = 7.77$, $b = 8.45$, $c = 10.47$ Å. The number of molecules per unit cell is 4. The space group is $P2_12_12$. The crystals of p-xylene belong to the monoclinic system with $a = 7.56$, $b = 8.45$, $c = 11.11$ Å, $\beta = 98° 57'$. The number of molecules per unit cell is 4. The space group is $P2_1/m$.

INTRODUCTION

In continuation of the previous work on the analysis of the Debye-Scherrer patterns of crystals of toluene (Biswas and Sirkar, 1957), pyridine (Biswas, 1958), chlorobenzene and bromobenzene (Biswas, 1958) and 1, 3, 5-trichlorobenzene (Biswas, 1959) the present investigation was undertaken to study the Debye-Scherrer patterns of o-xylene, m-xylene and p-xylene in the frozen state at −180°C to find out the dimensions of the unit cell, number of molecules per unit cell and the space group. Such data throw much light on the influence of intermolecular field on the individual molecules and are helpful in understanding the changes which take place in the electronic spectra of these molecules with the change from the liquid to the solid state.

EXPERIMENTAL

The chemicals o-xylene, m-xylene and p-xylene used in the investigation were of chemically pure quality supplied by Fisher and Co.. Debye-Scherrer patterns of the substances were taken with a low-temperature camera of special design discussed earlier (Biswas, 1958). The radius of the camera was derived from the Debye-Scherrer pattern of Al powder, and it was found to be

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4.50 cm.   The specimen in the form of liquid was introduced in a Lindemann glass capillary tube of bore 0.3mm and frozen with liquid oxygen.   A Seifert X-ray tube running at 32 Kv and 26 mA was used to photograph the patterns.   An exposure of three and a half hours was sufficient to record the pattern with appropriate density, using Cu K_a radiation. The densities of the frozen substances at $-180°C$ were measured by the method described earlier (Biswas and Sirkar, 1957).   For the ortho variety the density was found to be 1.030 gm cm^{-3}, for the para compound 1.006 gm cm^{-3}, and for the meta compound 1.030 gm $cm.^{-3}$.

RESULTS AND DISCUSSION

(a)   *Meta-xylene at* $-180°C$:

The Debye-Scherrer pattern is reproduced in Fig. 1, Plate IV. In the determination of unit cell dimensions of ortho, meta and para xylene from the Debye-Scherrer patterns, Lipson's method (Lipson, 1949) was first tried and when this method showed the lattice to be other than orthorhombic, Ito's method (Ito, 1950) was applied.   The patterns could not be assigned to any lattice having a symmetry higher than that of the orthorhombic.

The values of $\sin^2\theta$ for the rings in the Debye-Scherrer pattern due to m-xylene crystals are given in column 1 of Table I, and with these values the difference diagram was drawn according to Lipson's method.   It was found from the diagram that the determination of the values of A, B, C from the equation

$$\text{Sin}^2\theta = Ah^2 + Bk^2 + Cl^2 \qquad \qquad ... \quad (1)$$

$$(A = \lambda^2/4a^2, \quad B = \lambda^2/4b^2 \quad C = \lambda^2/4c^2).$$

was quite easy and all the rings could be indexed quite satisfactorily.   The values of A, B, C determined in this way are A = .0098, $B = .0083$ and C = .0054.   The axial lengths calculated from these values of A, B, C are : $a = 7.77,\ b = 8.45,\ c = 10.47$ Å.   The values of $\sin^2\theta$ calculated with · these axial lengths, the intensities of the Debye—Scherrer rings, the spacings and the indices are given in TableI, and it can be seen that the discrepancies between the calculated and observed values lie within the experimental error.

With these values of the dimensions of the unit cell and the value of the density determined in this investigation the number of molecules per unit cell was calculated and found to be 4.

The conditions limiting possible reflections indicated by Table I are

$$\left.\begin{matrix} hkl \\ hko \\ hol \\ oko \end{matrix}\right\} \quad \text{No condition} \quad \begin{matrix} hoo : h = 2n \\ ool : l = 2n \end{matrix}$$

Fig. 1.

Fig. 2 (a).

Fig. 2 (b).

Fig. 3.
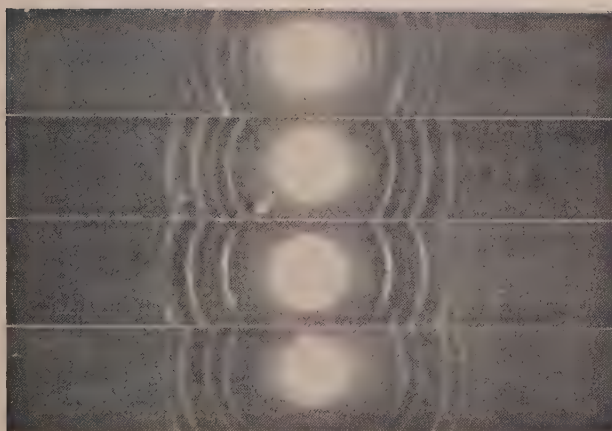
Fig. 1,   Debye-Scherrer pattern of frozen *m*-xylene at −180°C
Fig. 2 (a). Fibre like pattern of frozen *o*-xylene at −180°C
Fig. 2 (b). Debye-Scherrer pattern of frozen *o*-xylene at −180°C
Fig. 3.   Debye-Scherrer pattern of frozen *p*-xylene at −180°C

TABLE I

m-Xylene at −180°C

sin $^2\theta$ (observed)	sin $^2\theta$ (calculated)	Spacings (Å) (observed)	Indices
.0083 (s)	.0083	8.45	010
.0137 (s)	.0137	6.58	011
.0184 (vw)	.0181	5.68	110
.0215 (m)	.0216	5.24	002
.0236 (m)	.0235	5.02	111
.0302 (m)	.0299	4.43	012
.0330 (w)	.0332	4.24	020
.0392 (s)	.0392 .0397	3.89	200 112
.0478 (m)	.0475 .0484	3.52	210 121
.0530 (w)	.0529	3.34	211
.0547 (w)	.0548	3.25	022
.0606 (m)	.0608	3.13	202
.0648 (vw)	.0646	3.02	122
.0750 (vw)	.0747	2.81	030
.0801 (m)	.0801	2.72	031
.0865 (m)	.0864	2.62	004
.0938 (vw)	.0936 .0940	2.52	301 222
.1020 (vw)	.1019	2.41	311
.1170 (w)	.1173	2.25	231
.1290 (w)	.1294	2.14	124
.1332 (m)	.1328 .1339	2.11	040 214
.1430 (w)	.1430 .1433	2.04	322 015
.1484 (w)	.1480	2.00	141
.1427 (w)	.1430	1.97	115
.1572 (vw)	.1568	1.94	400
.1746 (m)	.1746	1.84	304

Since the crystal belongs to the orthorhombic system and the unit cell contains molecules, the crystal belongs to the space group $P2_1 2_1 2$ or D_2^3.

It can be seen from the above discussions that the number of molecules in the unit cell is the same as that required in the case of asymmetric molecules. The molecule may have either a plane of reflection perpendicular to its plane or a two-fold axis in its own plane. The plane cannot be utilised in the space group mentioned above and it is evident that the two-fold axis, it if is actually possessed by the molecule, does not coincide with any of the crystallographic axes.

(b)   *Ortho-xylene at* $-180°C$:

One of the many Debye-Scherrer patterns photographed for frozen o-xylene was found to be analogous to a pattern due to a fibre while the other photographs showed continuous rings.   Figs. 2(a) and 2(b) plate III show these two types of photographs.   The former type helped the correct assignment of the indices.

Lipson's method applied in this case also indicated the lattice to be orthorhombic.   It was found, however, that while two of the axial lengths were identical with those for the *m*-xylene lattice, the primitive translation along the third axis had to be taken as almost double that for the meta compound in order to index all the reflections in the powder pattern.

The values of $\sin^2\theta$ observed in the pattern and those calculated from the values of A, B, C determined from the difference diagram, the spacings and the indices are given in Table II.   It can be easily seen from Table II that the agreement between the observed and the calculated values of $\sin^2\theta$ is very satisfactory. The correctness of the indices has been verified by examining the positions of the maxima in the rings due to the fibrous specimen [Fig. 2(b)].   The values of A, B, C in this case are A = .0028, B = .0077, C = .0057, from which the dimensions of the unit cell have been calculated and found to be $a = 14.55$, $b = 10.20$ and $c = 8.77$ Å.

From the value of the density mentioned earlier and the axial lengths given above the number of molecules per unit cell was calculated and found to be 8. The values of $\sin^2\theta$ and the indices of the corresponding planes given in Table II show that there is no restriction limiting any reflection.   So, the space group assigned to the crystal is Pmmm or D_2^1.

The molecule of o-xylene may have a plane of reflection perpendicular to the plane of the molecule and a two-fold axis in the plane of the molecule if the two CH_3 groups in the molecule form mirror images of each other in a vertical plane between them owing to their mutual orientation produced by steric repulsion. If the plane were parallel to any of the crystallographic plane the number of molecules per unit cell would be reduced to 4, but actually the number is 8.

Hence the plane of the molecule is inclined to the crystallographic axis forming a complicated structure.

TABLE II

o-Xylene at −180°C

$\sin^2 \theta$ (observed)	$\sin^2 \theta$ (calculated)	Spacings (Å) (observed)	Indices
.0076 (ms)	.0077	8.83	100
.0086 (ms)	.0085	8.30	011
.0112 (vw)	.0111	7.28	002
.0162 (vw)	.0162	6.09	111
.0170 (vs)	.0168	5.90	012
.0228 (s)	.0228	5.10	020
.0248 (s)	.0245	4.89	112
	.0250		003
.0310 (vs)	.0308	4.37	200
.0338 (vs)	.0336	4.19	201
	.0339		022
.0442 (s)	.0445	3.66	004
.0478 (s)	.0476	3.52	212
.0507 (m)	.0502	3.42	014
	.0512		300
.0574 (m)	.0579	3.21	114
.0644 (w)	.0646	3.03	222
.0724 (vw)	.0721	2.86	301
.0812 (s)	.0810	2.70	214
.0866 (w)	.0862	2.62	312
.0916 (vw)	.0914	2.54	040
.1034 (ms)	.1033	2.40	322
	.1035		134
.1174 (ms)	.1171	2.25	323
.1314 (ms)	.1310	2.12	206
.1438 (vs)	.1434	2.03	144
.1595 (vs)	.1591	1.93	136
.1778 (vs)	.1780	1.83	008
	.1773		431
.1835 (w)	.1837	1.80	018
.2012 (w)	.2008	1.72	028
	.2010		511
.2048 (w)	.2050	1.70	344
.2408 (vw)	.2403	1.57	523

(c) *paraxylene at* $-180°C$:

The Debye-Scherrer pattern is reproduced in Fig. 3. Plate I. In determining the dimensions of the unit cell of the para compound it was noticed that the difference diagram did not yield sufficient number of constant differences. Hence Ito's method (Ito, 1950) was applied to index the pattern.

In order to select the axial lengths a^*, b^*, c^* of the reciprocal unit cell it was observed that all the spacings of the planes hoo, oko, ool with h, k, l even observed in the case of the m-xylene crystal were also present in the Debye-Scherrer pattern due to the para compound. These reflections were first utilised in selecting the values of a^*, b^*, c^*. The values are :

$$a^{*2} = 1/d^2{}_{100} = .0083, \quad b^{*2} = 1/d^2{}_{010} = .0138, \quad c^{*2} = 1/d^2{}_{001} = . .0180$$

In order to select the reciprocal cell angles α^*, β^*, γ^*, (hko), (hol) and (okl) reflections were carefully examined and it was observed that some (hko) and (okl) reflections were present if the angles a^*/b^* and b^*/c^* were taken to be $90°$, and the angle a^*/c^* was calculated by studying some pairs of (hol) and $(ho\bar{l})$ reflections according to the equation

$$\cos\beta^* = \frac{1/d^2{}_{hol} - 1/d^2{}_{ho\bar{l}}}{4hla^*c^*} \qquad \ldots \quad (2)$$

where d_{hkl} is the spacing in the direct lattice.

Thus the reciprocal cell-dimensions were calculated and found to be

$$a^* = .0911 \qquad \qquad \alpha^* = 90°$$
$$b^* = .1174 \qquad \qquad \beta^* = 81°3'$$
$$c^* = .1339 \qquad \qquad \gamma^* = 90°$$

With these values of the cell dimensions all the reflections in the powder pattern of the para xylene crystals were indexed according to the equation

$$1/d^2{}_{hkl} = h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2hla^*c^* \cos\beta^* \qquad \ldots \quad (3)$$

and the agreement was found to be satisfactory. The values of $1/d^2$ observed from the photograph and those calculated with the help of Eqn.(3), the intensities, and the indices are given in Table III. The real cell corresponding to the reciprocal cell defines a lattice which is definitely the lattice of the crystal. The dimensions of the cell are

$$a = 7.56 \text{ Å}$$
$$b = 8.45 \text{ Å}$$
$$c = 11.11 \text{ Å}$$
$$\beta = 98°57'$$

TABLE III

p-Xylene at −180°C

$1/d^2$ (observed)	$1/d^2$ (calculated)	Indices
.0224 (vw)	.0225	$10\bar{1}$
	.0221	110
.0301 (s)	.0301	101
.0332 (m)	.0332	200
.0366 (w)	.0363	111
.0437 (m)	.0436	$20\bar{1}$
	.0439	111
.0470 (s)	.0470	210
.0550 (vs)	.0552	020
.0720 (vs)	.0722	002
.0730 (w)	.0732	$02\bar{1}$
	.0729	102
.0813 (w)	.0813	$30\bar{1}$
.0886 (vs)	.0884	220
	.0885	310
	.0881	$10\bar{2}$
.0900 (vs)	.0902	202
.0994 (w)	.0998	221
.1032 (w)	.1031	301
.1138 (s)	.1140	221
.1204 (w)	.1206	202
.1242 (s)	.1241	$30\bar{2}$
.1324 (m)	.1328	400
.2066 (s)	.2065	501
	.2060	$30\bar{3}$
.2208 (w)	.2208	040
	.2212	421
	.2213	510
	.2207	023
	.2215	203
.2432 (vw)	.2433	141
.2595 (vw)	.2593	511
.2750 (vw)	.2744	303
.2925 (s)	.2930	042
.3116 (vw)	.3110	$24\bar{2}$
	.3126	610
.3445 (vw)	.3440	024
.3608 (w)	.3608	$40\bar{4}$
.3830 (w)	.3834	143

Now it has to be found out whether this cell can be reduced further.

3-a

Let the primitive cell in the direct lattice have edges a, b, c written in order of increasing dimensions. corresponding to reciprocal lattice obtained from Ito's method. Every translation t in the real lattice can be written in the form

$$t = u\boldsymbol{a} + v\boldsymbol{b} + w\boldsymbol{c}$$

where u, v, w are integers. positive or negative. The problem of finding out the reduced cell is simply that of finding three shortest non-coplanar t's with the values of a, b, c determined from a^*, b^*, c^* and β^*. These three t's then become the edges of the reduced cell. This can be easily done by computation after assigning different values to u, v, w. both positive and negative. and it has been found that the arbitrary cell itself. initially chosen for indexing the pattern. is the reduced cell. Again. since the edges of a reduced face of a unit cell in the direct lattice are the shortest translations of the net. they are shorter than either of the two diagonals of the cell. For this reason the projection of either of the cell edges on the other cannot be greater than half the other edge (Buerger, 1957). As a consequence of this it follows that in a reduced plane cell,

$$\left| a \cos \gamma \right| \leqslant \frac{b}{2} \quad \text{and} \quad \left| b \cos \gamma \right| \leqslant \frac{a}{2}$$

$$\left| ab \cos \gamma \right| \leqslant \frac{b^2}{2} \quad \text{and} \quad \left| ab \cos \gamma \right| \leqslant \frac{a^2}{2}$$

These relations also apply to the reduced three-dimensional cell.

The six scalar products $\boldsymbol{a} \cdot \boldsymbol{a}$, $\boldsymbol{b} \cdot \boldsymbol{b}$, $\boldsymbol{c} \cdot \boldsymbol{c}$, $\boldsymbol{b} \cdot \boldsymbol{c}$, $\boldsymbol{c} \cdot \boldsymbol{a}$, $\boldsymbol{a} \cdot \boldsymbol{b}$ have been taken as an exact representation of the cell. since the six parameters a, b, c, α, β, γ can readily be derived from them. For the purpose of identification. these six scalar products are set down in a form of rectangular matrix to represent the reduced cell as follows :

$$\begin{pmatrix} \boldsymbol{a} \cdot \boldsymbol{a} & \boldsymbol{b} \cdot \boldsymbol{b} & \boldsymbol{c} \cdot \boldsymbol{c} \\ \boldsymbol{b} \cdot \boldsymbol{c} & \boldsymbol{c} \cdot \boldsymbol{a} & \boldsymbol{a} \cdot \boldsymbol{b} \end{pmatrix} = \begin{pmatrix} s_{11} & s_{22} & s_{33} \\ s_{23} & s_{31} & s_{12} \end{pmatrix}$$

Matrix representation of the direct cell of p-xylene crystal is found to be

$$\begin{pmatrix} 57.15 & 71.42 & 123.40 \\ 0.00 & -12.92 & 0.00 \end{pmatrix} \qquad \dots \ (7)$$

From representation (7) it can be seen that $\boldsymbol{a} \cdot \boldsymbol{c}$ is less than either $\frac{1}{2} \boldsymbol{a} \cdot \boldsymbol{b}$ or or $\frac{1}{2} \boldsymbol{b} \cdot \boldsymbol{b}$. Hence according to (5) no further reduction is possible. From (7) it can also be seen that $s_{11} = s_{22} \neq s_{33}$. and since zero is regarded as negative ($90°$ is regarded as obtuse angle for the purpose of identification) the standard cell is a primitive monoclinic one as indicated by Azaroff and Buerger (1958). With

the values of the dimensions of the unit cell given earlier and the density of the substance at ‑180°C determined experimentally the number of molecules per unit cell has been calculated and found to be 4.

The conditions limiting possible reflections for p-xylene crystals are

$$hkl : \text{No condition}$$
$$hol : \text{No condition}$$
$$oko : k = 2n$$

So the space group $P2_1/m$ has been assigned to the crystal.

The p-xylene molecule may have a plane of symmetry perpendicular to the plane of the molecule and also a centre of symmetry with the two CH_3 groups oriented in a particular way. As regards the plane of reflection this particular space group cannot utilise the symmetry element as in that case the number of molecules would be reduced to two. Again, the contribution of the hydrogen atom in X-ray scattering is almost negligible. Therefore, the centre of symmetry could have been utilised by the molecule to form the lattice and in that case the number of molecules per unit cell would be 2. Actually, however, the unit cell contains 4 molecules. Hence it appears that the molecule does not possess the centre of symmetry in the solid state at −180°C.

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ULTRASONIC VELOCITY IN SUPERCOOLED LIQUIDS

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ABSTRACT. Velocity of ultrasonic waves has been studied over a range of temperatures extending into the supercooled region in five liquids, viz., thymol, phenol, salol, benzophenone, and diphenylamine.

It is observed that the temperature coefficient of velocity $1/v$ (dv/dt), does not remain the same on either side of the melting points in thymol and benzophenone. Salol, diphenylamine and benzophenone show a small abrupt change in velocity values as the melting point is crossed. These changes are attributed to possible structural changes encountered during transition from the liquid to the super-cooled state, which must be associated with the corresponding change of adiabatic compressibility. Phenol does not show any discontinuity and the gradient is also the same over the whole range. As phenol is highly hygroscopic it is likely to be mixed with certain amount of water and preseumably the presence of water masks the small variation in temperature gradient if any.

INTRODUCTION

The characteristic behaviour of many liqui d s in passing from the normal state to supercooled state has been studied with respect to the various physical properties such as viscosity ((Dodd and Hu,→1949) dielectric constant (Dodd and Roberts, 1950) density (Greenwood and Martin, 1952) specific heat, surface tension (Dodd, 1951) and vapour pressure. Ultrasonic velocity (Barone *et al.*, 1957) and absorption (Hunder, 1951; Parthasarathy and Bindal, 19 0) have also been studied to some extent on certain liquids over various ranges of temperatures.

According to Barone, Pisent and Sette some polar liquids which can be easily supercooled show a sudden change of activation energy since viscous flow occures at a temperature near melting point. They attribute this change to some structural variation inside the liquid.

Hunter (1951) worked on menthol and Petra and Cevolain (1951) in salol. Hunder observed a slight variation of temperature co-efficient in menthol but Petra and Cevolain were not able to detect this effect in salol.

Subsequently, Barone, Pisent and Sette (1957) have investigated, menthol dippenyl ether, *m*-chloronitrobenzene and salol in the normal and supercooled regions. They have discussed the results on the basis of viscosity measurement

and explained that the structural variation, which might be responsible for the variation in temperature co-efficient in the two states of liquid are mainly due to formation of molecular associations.

The present work was undertaken to study some more liquids and to investigate their behaviour with respect to ultrasonic propagation in the temperature range of 30°C to 70°C, the melting point of the liquids in question being in the region of 50°C. With the help of a precision interforemeter the ultrasonic velocity was measured in salol, thymol, benzophenone, diphenylamine and phenol,

<div align="center">EXPERIMENTAL</div>

The work under report was done at a frequency of 6 Mcs.. The r.f. generator used consisted of 2 Mcs crystal controlled oscillator in the form of a modified Pierce oscillator. This was followed by an amplifier tripler stage giving 6 Mcs. The r.f. output was fed to the load crystal fixed at the bottom of the interferometer through a condenser coupling. The H. T. current to the output tube was fed through a bridge net-work including a microammeter in such a way that changes in the plate current could be easily observed on the microammeter.

A precision interferometer was used for finding out the velocity at different temperatures by measuring the half wave-length in the liquid under test by shifting the reflector plate with the help of a micrometer screw.

If sound waves proceeding from a vibrating quartz are incident on plane reflector parallel to the source a standing wave pattern is obtained. The plate current of the output tube registers a change depending on the reaction on the transducer produced by a reflected wave. This reaction is maximum when the reflected wave returns 180° out of phase with the out going wave in which case the plate current shows a maximum dip. As the position of the reflecting plate is further changed the reaction on the generator passes through a maximum for each $\lambda/2$ path difference of sound waves corresponding to movement of the reflector. The reflector movements can be very accurately read with the help of micrometer screw driving it. In the electric circuit, the bridge network is so adjusted for maximum sensitivity that the dips in the current can be easily counted as the reflector plate is moved. The total distance travelled by the reflector divided by the number of dips gives the value of half the wave length. Knowing the frequency of the oscillator the velocity can be calculated.

For the measurement of the velocity at different temperatures, water, from a thermostatically controlled bath was circulated around the liquid under experiment in the interferometer with the help of a centrifugal pump and the temperature was recorded with the help of 1/10°C. thermometer, the temperature was constant within 0.1°C.

The arrangement gives .05% as the accuracy in velocity measurement.

3-b

RESULTS AND DISCUSSION

The results obtained in salol, thymol, benzophenone, diphenylamine and phenol are given in Figs. 1, 2, 3, 4 and 5 respectively. They have also been placed in a tabular form for comparison.

It is noticed from the above results that in phenol (Figs. 5) there is no change in ultrasonic velocity as the temperature is reduced below the melting point into the supercooled region. The reason for this may be due to its hygroscopic nature, it is likely to be mixed with certain amount of water. Presumably the presence of this water masks the small variation in temperature gradient if any in phenol.

TABLE I

Comparison of velocity (M/sec) in different liquids at different temperatures

S.No.	Temp. °C	Salol m.p.:42°C	Thymol m.p.:51.5°C	Benzo- phenone m.p.:48°C	Dipheny- lamine m.p.:54°C	Phenol m.p.:41°C
1	30	1463.00	1406.00	1544.00	1622.00	1485.00
2	33	1453.50	1396.00	1535.00	1611.00	1475.50
3	36	1444.00	1387.00	1526.00	1600.00	1466.00
4	39	1434.00	1378.00	1517.00	1589.00	1457.00
5	42	m.p.	1368.00	1508.00	1578.00	1448.00
6	45	1412.00	1359.00	1499.00	1567.00	1439.00
7	48	1402.50	1350.00	m.p.	1556.00	1429.50
8	51	1393.00	1240.75	1477.00	1545.00	1420.00
9	54	1383.50	1330.00	1465.50	m.p.	1411.00
10	57	1374.00	1320.00	1454.00	1417.75	1401.75
11	60	1364.75	1310.00	1442.50	1507.00	1392.25
12	63	1355.00	1300.00	1431.00	1496.00	1383.00
13	66	1346.75	1290.00	1419.25	1486.00	1374.00
14	69	1337.00	1280.00	1407.75	1475.00	1364.75
15	72	1228.00	1270.00	1396.50	1464.75	1355.50

In the case of thymol (Fig. 2) it is noticed that there is no appreciable abrupt change in the velocity near the melting point but the temperature co-efficient of velocity is different on either side. Benzophenone, (Fig. 3) salol (Fig.1), and diphenylamine (Fig. 4) show a sudden change in velocity. In salol (Fig. 1) the change is about 11 meter as the temperature is lowered by about 2.5°C in the

neighbourhood of the melting point whereas the normal variation of velocity for 2.5°C change of temperature is found to be about 7 m only.
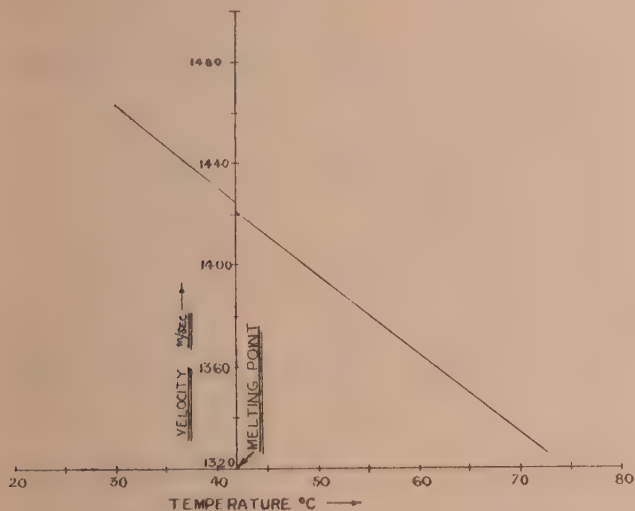

Fig. 1, Ultrasonic velocity in phenyl salicylate (salol).
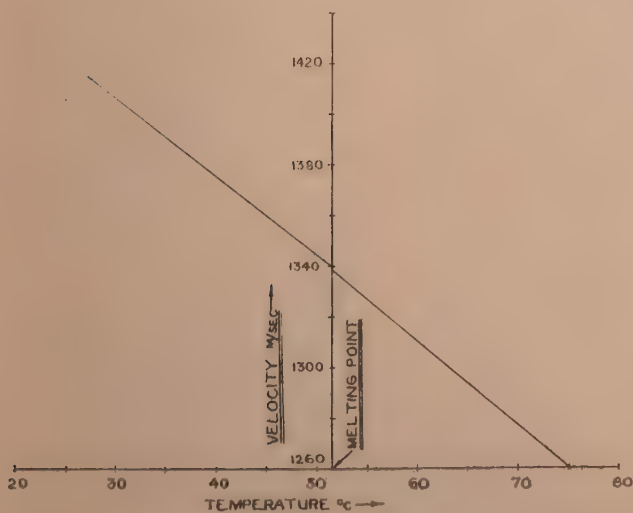

Fig. 2. Ultrasonic velocity in thymol.

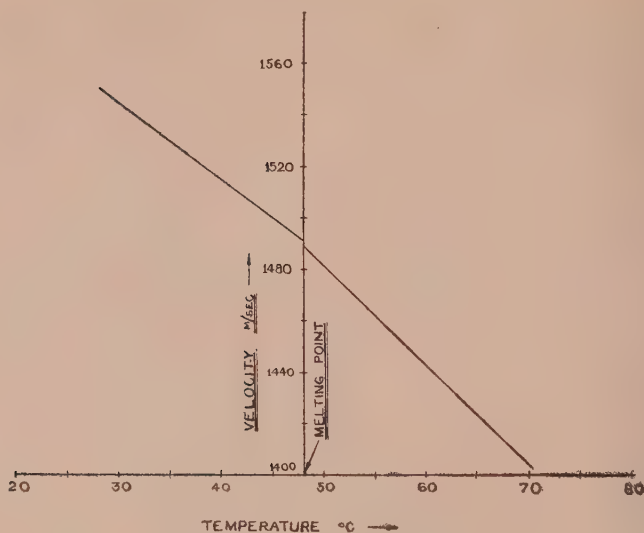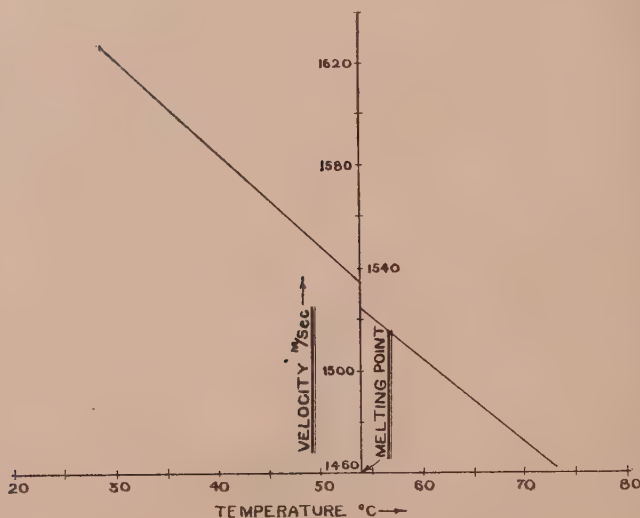Fig. 3.   Ultrasonic velocity in benzophenone.

Fig. 4.   Ultrasonic velocity in diphenylamine.

The curve obtained in salol (Fig. 1) in the present case does not agree with the curve obtained by Barone and Pisent (1957)·   They have reported that in the neighbourhood of the melting point, the velocity is changing from higher to lower values as the temperature is lowered to supercooled region whereas in the
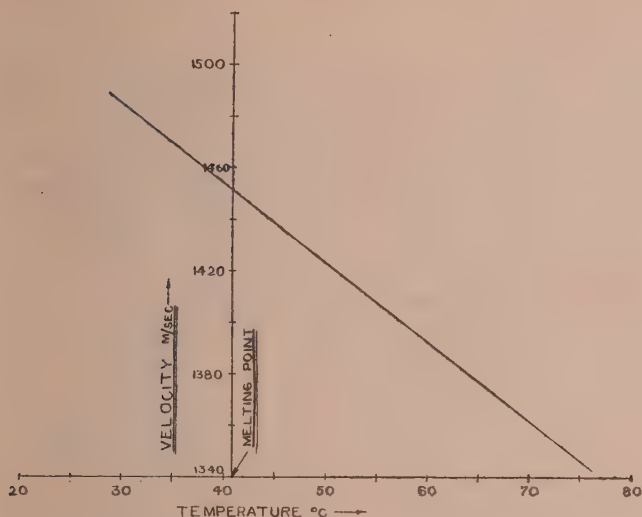
Fig. 5. Ultrasonic velocity in carbolic acid (phenol).

other liquids studied by them give the reverse order. In the work under report not only benzophenone and diphenylamine but also salol show an abrupt increase of velocity as the temperature is lowered to cross the melting point. Presently, it may be explained that the variation in the values in the two regions may be due to structural changes which take place in liquid from normal to supercooled state. Any change in the structure is likely to be associated with a corresponding change of adiabatic compressibility. Dodd (1949) working on measurement of densities of various supercooled liquids observed no detectable change in the temperature-co-efficient of density. This again indicates that the adiabatic compressibility must show an abrupt change at the melting point of the liquids. In the present case if the densities of these liquids are also measured over a similar range of temperature extending into the supercooled region it would be possible to calculate the actual adiabatic compressibility from velocity data aldready obtained. Work on other lines is in progress.

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ULTRAVIOLET BAND SPECTRA OF AsO AND AsO⁺

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Plate V

ABSTRACT. The band spectrum of AsO was excited, in a heavy current discharge from a 4 K.V. transformer, using a quartz discharge tube with internal hollow nickel electrodes fed with a specpure sample of As_2O_3. Two new doublet systems of bands designated as $C-X^2\Pi$ and $D-X^2\Pi$, analogous to those reported by one of the authors (Lakshman 1960) in the case of SbO, were observed in the region $\lambda\ 3100-\lambda\ 2400$ A°. The spectra were photographed on a Hilger medium quartz and E_1 quartz littrow spectrographs. Vibrational analyses of these systems were carried out leading to the following quantum formulae :

$$C-X^2\Pi: \quad \nu = \left.\begin{array}{c} 38637.1 \\ 37664.8 \end{array}\right\} +656.3(\nu'+\tfrac{1}{2})-4.85(\nu'+\tfrac{1}{2})^2-964.0(\nu''+\tfrac{1}{2})+4.50(\nu''+\tfrac{1}{2})^2$$

$$D-X^2\Pi: \quad \nu = \left.\begin{array}{c} 38805.9 \\ 37780.5 \end{array}\right\} +611.5(\nu'+\tfrac{1}{2})-3.338(\nu'+\tfrac{1}{2})^2-964.0(\nu''+\tfrac{1}{2})+4.50(v''+\tfrac{1}{2})^2$$

In addition to the above systems, a singlet system of bands was obtained in the region $\lambda\ 2550-\lambda\ 2200$ Å. A vibrational analysis of this system gave the following constants.

$$\nu_e = 42601.1 \text{ cm}^{-1} \qquad \begin{array}{ll} \omega_e' = 777.0. \text{ cm}^{-1} & x_e'\omega_e' = 6.57 \text{ cm}^{-1} \\ \omega_e'' = 1100.4 \text{ cm}^{-1} & x_e''\omega_e'' = 4.878 \text{ cm}^{-1} \end{array}$$

From the magnitude of the vibrational constants, it is concluded, that the emitter of this system is the hitherto unknown AsO⁺ ion.

Detailed arguments are presented for assigning this system to AsO⁺. The observed electronic states of AsO and AsO⁺ are compared and discussed with those of the related molecules on the basis of M.O. electron configurations.

INTRODCUTION

Connelly (1934), Jenkins and Strait (1935), Shawhan and Morgan (1935) reported two doublet systems $A-X$ and $B-X$ of AsO, in emission, in various sources of excitation in the region $\lambda 3450-\lambda 2350$ Å. Vibrational analyses of these two systems showed that they have a common lower state identified as a $^2\Pi$ state, with a doublet splitting of 1026 cm⁻¹. That this state is the normal state of the AsO molecule, is confirmed by the observation of the B—X bands in absorption by Connelly. Of these two systems the A—X system consists of red degraded bands in the region $\lambda 3450-\lambda 2950$ Å while the B—X comprises of violet degraded bands in the region $\lambda 2800-\lambda 2350$ Å. From the observed double—

double headed nature of the bands, each of the two systems was ascribed to a $^2\Sigma - ^2\Pi$ transition.

The present investigations on the spectrum of AsO in heavy current discharges were started with a view to obtain possible new systems analogous to the C—X and D—X systems of SbO previously reported by one of the authors (Lakshman 1960). This work has led to the analysis and identification of two new doublet systems designated as C—X$^2\Pi$ and D—X$^2\Pi$ of the AsO molecule and of a band system attributable to the molecule AsO$^+$ whose existence is spectroscopically hitherto unknown. We describe below the experimental procedure and the results of detailed analysis of the ultraviolet band systems of AsO and AsO$^+$.

EXPERIMENTAL

The spectra were excited in a heavy current discharge from a 4K.V. transformer, using a quartz discharge tube with internal hollow nickel electrodes fed with a specpure sample of As$_3$O$_3$. Photographs of the spectra were obtained under (a) low pressure stagnant vapour conditions by closing a stop-cock connected in between the dicharge tube and the system of evacuating pumps and (b) low pressure flowing vapour conditions. In the former case, the band spectrum of AsO was obtained in the region $\lambda3500- \lambda2400$ Å while in the latter case, a new group of bands attributed to the AsO$^+$ molecule was obtained in addition to the above. Exposures varying from three to ten minutes on Hilger medium quartz and one to two hours on E$_1$ quartz littrow spectrographs were found adequate to photograph the spectra on Ilford Selo-chrome and Special Rapid plates. The band heads were measured against iron arc standard lines, using a Hilger comparator.

RESULTS

AsO : *New systems* :

In addition to the A$^2\Sigma - X^2\Pi$ and B$^2\Sigma - X^2\Pi$ systems of AsO analysed by previous workers, the spectra reproduced in Plate V Figs. 1(a) and 1(b), reveal new groups of red degraded bands in the region $\lambda3100 \cdot \lambda2400$ Å. The new bands, start from the shorter wavelength side of the A—X system, and partly occur in a region of overlap with the B—X bands. The wave numbers, intensities, and the vibrational assignments for these bands are given in Table I.

Vibrational quantum formulae were derived for the Q—heads of the A—X and B—X systems by Connelly (1934) and also by Jenkins and Strait (1935).

We have observed that the new group of red degraded bands could not be fitted into the vibrational schemes of either of the two components of the A—X system. It seemed, therefore, reasonable to assume tha tthey constitute one or more new doublet systems of AsO molecule. A clue to the analysis of the new bands was obtained by the observation of progressions of bands, whose $\Delta G(r)$

TABLE I

Wavenumber, intensity and vibrational assignments for the bands of $C-X^2\Pi$ and $D-X^2\Pi$ syxtems of AsO and $A^1\Sigma-X^1\Sigma$ system of AsO$^+$

Wave-number cm^{-1}	Int.	v',v''	Wave-number cm^{-1}	Int.	v',v''	Wave-number cm^{-1}	Int.	v',v''
AxO C$-$X$^2\Pi_{3/2}$			AsO D$-$X$^2\Pi_{3/2}$			AsO$^+$ A$^1\Sigma-$X$^1\Sigma$		
33477	2	1,5	33839	2	0,4	39195	5	0,3
33745	3	0,4	35703	3	0,2	40267	7	0,2
34395	3	1,4	36448	4	0,1	41348	5	0,1
34673	4	0,3	37256	2	1,1	42113	8	1,1
35028	1	2,4	37602	4	0,0	42439	4	0,0
35609	7	0,2	38209	4	1,0	42866	2	2,1
35958*	–	2,3	38807	2	2,0	43205	6	1,0
36257	2	1,2	39402	2	3,0	43957	5	2,0
36558	7	0,1	AsO D$-$X$^2\Pi_{1/2}$			44693	3	3,0
37202	6	1,1	36727	2	0,2	45420	3	4,0
37843	4	2,1	37674	4	0,1			
38159	9	1,0	38280	3	1,1			
38794	4	2,0	38630	3	0,0			
39422	2	3,0	39236	5	1,0			
AsO C$-$X$^2\Pi_{1/2}$			39834	6	2,0			
34716	3	0,4	40424	4	3,0			
35644	4	0,3	41010	3	4,0			
36583	6	0,2	41588	3	5,0			
37531	8	0,1						
38180	2	1,1						
38487	4	0,0						

* Coincides with an atomic line.

intervals agree closely with those of the ground state X $^2\Pi$ of the AsO molecule. A detailed analysis, has shown that the new group of bands in the region $\lambda3100-\lambda2400$ Å could be interpreted on the basis of two overlapping doublet systems of bands, having a common lower state, identified as the X $^2\Pi$ state of the AsO molecule. On this basis, the bands have been arranged into two vibrational schemes shown in Tables II and III. Table II refers to the scheme of classification of a doublet system designated as C$-$X $^2\Pi$. As the bands appea.

single headed, they may be either the Q—heads of a $^2\Delta(a)$ $^2\Pi(a)$ transition or the R—heads of a $^2\Pi(a)$ $-^2\Pi(a)$ transition. Of the two possibilities, the former appears more likely as the upper state can be identified to be a $^2\Delta_a$ state from a comparison of this state with similar levels identified in NS, SiF and SbO. (See discussion below). As the corresponding bands of the two component systems are separated by ~970 cm⁻¹ the upper state is a regular state and has a doublet splitting equal to $1026-970 = 56$ cm⁻¹. The C X $^2\Pi_1$ component system consists of only the strong $v' = 0$ progression of bands. The bands heads of C—X $^2\Pi$ system could be represented by the quantum formula :

$$\nu = \left.\begin{matrix} 38637.1 \\ \\ 37664.8 \end{matrix}\right\} +656.3(v'+\tfrac{1}{2})-4.85\ (v'+\tfrac{1}{2})^2-964.0(v''+\tfrac{1}{2})+4.50(v''+\tfrac{1}{2})^2$$

to within an accuracy of 3 cm⁻¹.

TABLE II

Vibrational scheme of band heads of the $C-X^2\Pi$ system of AsO

v' \\ v''	0	1	2	3	4	5
0	38487	37531	36583	35644	34716	
		956	948	939	928	
	—	36558	35609	34673	33745	
			949	936	928	
		649	—		—	
		644	648		650	
1	—	38180	—	—	—	—
	38159	37202	36257	—	34395	33477
		957	945			918
	—	—	—	—	—	—
	635	641	—		633	
2	—	—	—	—	—	—
	38794	37843	—	35958	35028	
		951			930	
	—					
	628					
3	—					
	39422					

Table III shows the scheme of classification of band heads of the other doublet system designated as D—X $^2\Pi$. The analysis shows that the upper state D belongs to Hund's Case (b) and the lower state has a doublet splitting of 1026 cm⁻¹, which is identical with the doublet splitting of the $^2\Pi$ ground state. The bands

of this system also appear single headed and may be either the R heads of a $^2\Pi(b)-^2\Pi(a)$ transition, or the Q—heads of a $^2\Delta(b)-^2\Pi(a)$ transition.

The band heads of the two component systems could be represented by the quantum formula :

$$\nu = \left.\begin{array}{c} 38805.9 \\ 37780.5 \end{array}\right\} +611.5(v'+\tfrac{1}{2})-3.338(v'+\tfrac{1}{2})^2-964.0(v''+\tfrac{1}{2})+4.50(v''+\tfrac{1}{2})^2$$

to within an accuracy of 3 cm^{-1}.

AsO^+ :   *A singlet system* :

TABLE III

Vibrational scheme of Band heads of the $D-X^2\Pi$ system of AsO

v' \\ v"	0		1		2	3	4
0	38630	956	37674	947	36727	—	—
	37602	954	36648	945	35703	—	33839
	606		606				
	606		606				
1	39236	956	38280				
	38209	953	37256				
	598						
	598						
2	39834						
	38807						
	590						
	595						
3	40424						
	39402						
	586						
	—						
4	41010						
	—						
	578						
	—						
5	41588						
	..						

As was mentioned previously this system of bands was obtained in the region $\lambda 2550-\lambda 2200 \text{Å}$ when the vapour of a sample of As_2O_3 was kept flowing under low pressure conditions. It is reproduced in Fig. 1(c) of Plate V. The wave numbers, intensities, and the vibrational assignments for these bands are shown in Table I. The analysis of this system presented no difficulty. The two

progressions of bands $v'' = 0$ and $v' = 0$ were easily identified leading to the vibrational scheme displayed in Table IV. The following vibrational constants have been derived.

$$\omega_e' = 777.0 \ cm^{-1}$$

$$\nu_{s^{\prime\prime}} = 42601.1 \ cm^{-1} \qquad \omega_e'' = 1100.4 \ cm^{-1}$$

$$x_e'\omega_e' = 6.57 \ cm^{-1}$$

$$x_e''\omega_e'' = 4.878 \ cm^{-1}$$

TABLE IV

Vibrational scheme of AsO+ bands

v' \ v''	0		1		2		3
0	42439	1091	41348	1081	40267	1072	39195
	766		765				
1	43205	1092	42113				
	752		753				
2	43957	1091	42866				
	736						
3	44693						
	727						
4	45420						

The singlet structure of this system and a comparison of the vibrational constants of this system with those of NO+ and PO+ indicate that the emitter of this system is the hitherto unknown AsO+ ion. A detailed discussion on this is given in a later section.

DISCUSSION OF RESULTS

NO, PO, NS, PS, SiF, AsO and SbO :

We may now discuss the nature and properties of the electronic states of the AsO molecule in relation to those identified sofar in the spectra of the related molecules NO, PO, NS, PS, SiF and SbO. Fig. 2 gives the term scheme of electronic levels identified till now. The ground state of these molecules is well known to be a $^2\Pi$ state and is represented as X $^2\Pi$. The levels A, B, C, D etc., are arranged in the order of increasing energy. However, the designation of the levels in PO and NO is not strictly in the order X, A, B, C etc. We notice for instance, that the first and second excited states of PO are represented by B $^2\Sigma$ and A $^2\Sigma$ respectively, while the B' $^2\Delta_i$ term in NO occurs in between the D and E levels, and the new C and D levels in AsO fall in between A and B. The ratio

of the vibrational frequency of an excited state with respect to the ground state viz. $\dfrac{\omega_e'^{\frac{1}{2}}}{\omega_e''}$ is shown on the right. It gives us a measure of the relative strength of binding of the excited state with respect to the ground state as the square of this quantity gives the value of $\dfrac{k_e'}{k_e''}$ from the relation $k_e = 4\pi^2 c^2 \mu\, \omega_e^2$. The values
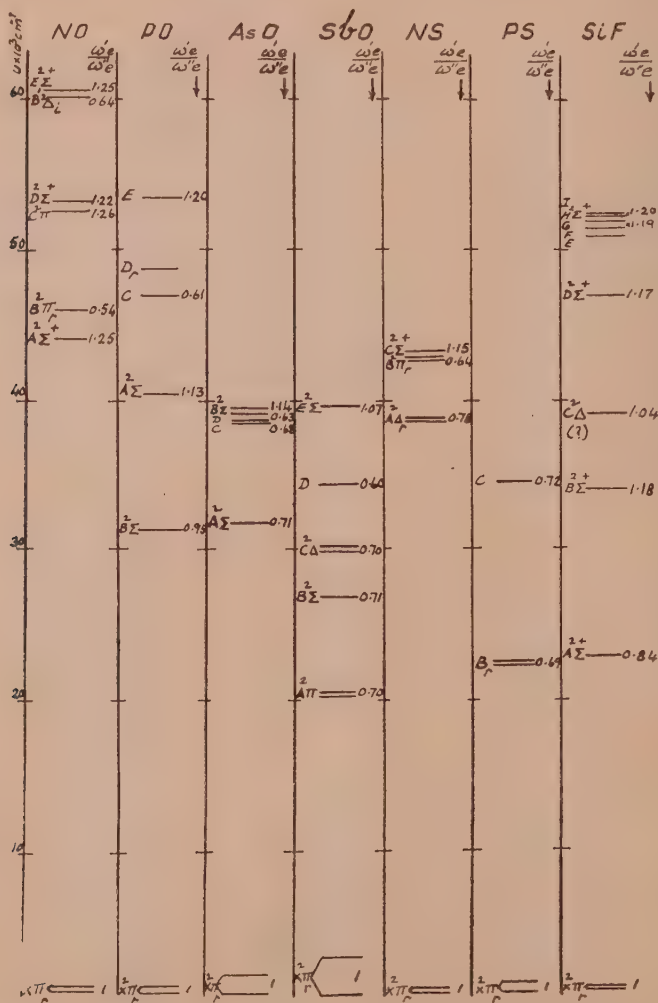

Fig. 2. Energy levels of NO, PO, AsO, SbO, NS, PS and SiF.

of $\dfrac{\omega_e'}{\omega_e''}$ and $\dfrac{k_e'}{k_e''}$ would be helpful in the identification of analogous states in the series of molecules referred above.
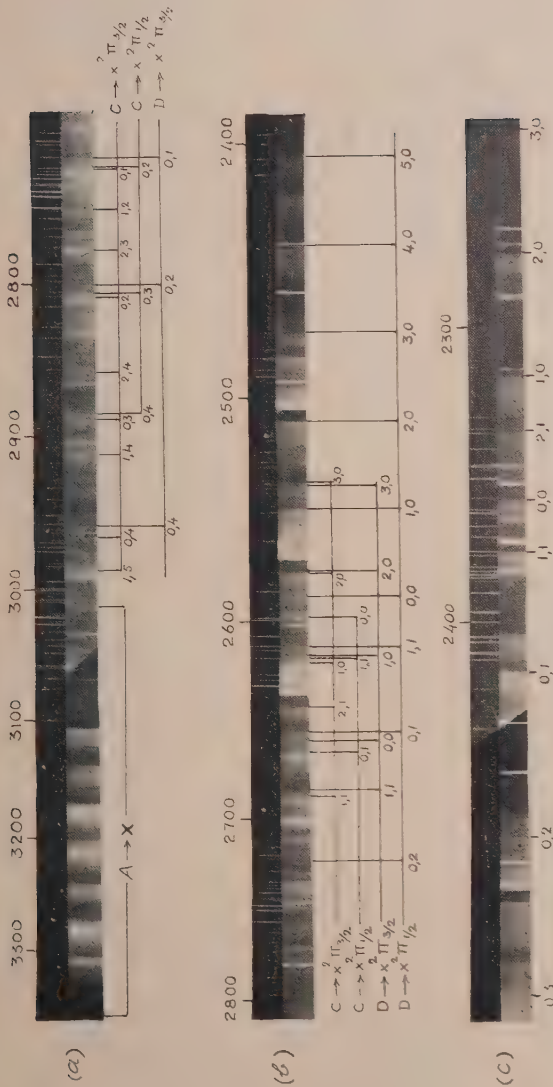
Fig. 1. Medium quartz spectrograms.

(a) and (b) : The new C—X and D—X systems of AsO

(c) : The A $^1\Sigma$—X $^1\Sigma$ system of AsO$^+$

(The violet degraded bands in (b) and (c) belong to the B—X system of AsO)

The observed molecular electronic states of NO, NS, PO, PS were previously discussed on the basis of expected molecular electron configurations by Dressler (1955), and of NS and SiF by Barrow (1954 and 1958). Leaving the completed K and L shells, the ground state configuration in these molecules, in Mulliken's notation, is represented as

$$...(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)^2(v\pi) ... \, {}^2\pi_r \qquad\qquad ... \, (1)$$

The results of a recent rotational analysis of PO by Singh (1959) and SiF by Johns and Barrow (1957) definitely show that the B level in PO $\left(\dfrac{\omega'_e}{\omega''_e} = 0.94 \right)$

and A level in SiF $\left(\dfrac{\omega'_e}{\omega''_e} = 0.84 \right)$ belong to a $^2\Sigma$ term. These states appear

analogous to the $A^2\Sigma$ level in AsO $\left(\dfrac{\omega_e'}{\omega_e''} = 0.71 \right)$ and $B\,{}^2\Sigma$ in SbO

$\left(\dfrac{\omega_e'}{\omega_e''} = 0.71 \right)$ and belong to the excited configuration

$$...(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)(v\pi)^2 ... \, {}^2\Sigma^+, \, {}^2\Sigma^-, \, {}^2\Delta, \, {}^4\Sigma^- \qquad\qquad ... \, (2)$$

The reduction in the vibrational frequency in the excited state of each of the molecules is due to the transition of an electron from the bonding $x\sigma$ orbital to the anti-bonding $v\pi$ orbital. However, as was mentioned by Dressler, the reduction in the vibrational fredquency of the $B\,{}^2\Sigma$ state in PO is not so large as in others, indicating that the $x\sigma$ orbital in PO is practically non-bonding.

In addition to the $^2\Sigma$ state discussed above, the above configuration also gives rise to a $^2\Delta$ term. This state was identified with the B' level in NO by Miescher (1956) and with A level in NS by Barrow, Drummond and Zeeman (1954). A comparison of the values of ω_e'/ω_e'' for these states with the observed C levels in AsO and SbO (Lakshman, 1960) reveal that all of them are analogous. We may thus assign the C levels in AsO and SbO to a $^2\Delta$ term arising from configuration (2).

The vibrational analyses of the $C-X\,{}^2\Pi$ in PO and of the $D-X^2\Pi$ system of AsO indicate that the upper state belongs to Hund's case (b). But the $\wedge$—value of the state remains unknown, in the absence of the results of a rotational analysis.

The B level in AsO, E in SbO, C in NS and B in SiF are analogous states. Each of these states is characterised by an increase in the vibrational frequency and thereby the force constant with respect to the ground state. These states belong to the configuration

$$... (z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)^2 .. (\sigma) ... \, {}^2\Sigma^+ \qquad\qquad ... \, (3)$$

corresponding to the transition of an electron from a $e\pi$ anti-bonding orbital to a non-bonding σ orbital.

NO+, NS+, PO+, PS+ and AsO+ :

In this section, we propose to give detailed reasons for assigning the singlet system reproduced in strip (c) of Plate V to the AsO+ ion. The arguments presented in the following discussion are closely similar to those used by Dressler (1955) in the spectroscopic identification of the ions NS+, PO+ and PS+. The justi-acation for attributing this singlet system to the AsO+ ion can be seen from the fact that there is a considerable increase in the vibrational frequency of the ground state term of the ion arising from the removal of the last $v\pi$ anti-bonding electron of configuration (1) representing the ground state of the neutral AsO molecule.

We compare in Table IV the values of $\dfrac{\omega_e'' \text{ (Ion)}}{\omega_e'' \text{(Molecule)}}$ and $\dfrac{k_e'' \text{ (Ion)}}{k'' \text{ (Molecule)}}$ for the pairs of molecules NO+, NO; NS+, NS; PO+, PO; PS+, PS; and AsO+, AsO.

We observe from the Table V that the values of $\dfrac{\omega_e'' \text{ (Ion)}}{\omega_e' \text{ (Molecule)}}$ and $\dfrac{k_e'' \text{ (Ion)}}{k_e'' \text{(Molecule)}}$ are exactly equal in the case of the three pairs of molecules given in the last three columns.

TABLE V

Comparison of the values of $\dfrac{\omega_e'' \text{ (Ion)}}{\omega_e'' \text{ (Molecule)}}$ and $\dfrac{k_e'' \text{ (Ion)}}{k_e'' \text{ (Molecule)}}$ for the pairs of molecules NO+, NO; NS+, NS; PO+, PO; PS+, PS; and AsO+, AsO.

	$\dfrac{\text{NO+}}{\text{NO}}$	$\dfrac{\text{NS+}}{\text{NS}}$	$\dfrac{\text{PO+}}{\text{PO}}$	$\dfrac{\text{PS+}}{\text{PS}}$	$\dfrac{\text{AsO+}}{\text{AsO}}$
$\dfrac{\omega_e'' \text{ (Ion)}}{\omega_e'' \text{ (Molecule)}}$	$\dfrac{2377}{1904} = 1.25$	$\dfrac{\times}{1219}$	$\dfrac{1405}{1233} = 1.14$	$\dfrac{845}{740} = 1.14$	$\dfrac{1100}{964} = 1.14$
$\dfrac{k_e'' \text{ (Ion)}}{k_e'' \text{ (Molecule)}}$	1.56	—	1.30	1.30	1.30

A similar comparison of the values of v_e and $\dfrac{\omega_e'}{\omega_e''}$ and $\dfrac{k_e'}{k_e''}$ (given in Table VI) for the ions NO+, NS+, PO+, PS+ and AsO+ also shows that there is a similar decrease in the strength of binding of the upper state relative to the ground state. The v_e values of the singlet systems show the expected shift towards red with

TABLE VI

The values of ν_e, $\dfrac{\omega_e'}{\omega_e''}$, and $\dfrac{k_e'}{k_e''}$ for the molecules NO⁺, NS⁺, PO⁺, PS⁺ and AsO⁺

i_n'	ν_e cm⁻¹	Transition	$\dfrac{\omega_e'}{\omega_e''}$	$\dfrac{k_e'}{k_e''}$
NO⁺	73470	$A^1\Pi - X^1\Sigma$	0.68	0.46
NS⁺	42000	$A^1\Pi - X^1\Sigma$	—	—
PO⁺	49930	$A - X$	0.73	0.53
PS⁺	40620	$A^1\Sigma - X^1\Sigma$	0.72	0.52
AsO⁺	42600	$A^1\Sigma - X^1\Sigma$	0.71	0.50

increasing value of μ, the reduced mass, as we pass from NO⁺ and PO⁺ to AsO⁺. Since the ground state arises from the configuration

$$\ldots (z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)^2 \ldots {}^1\Sigma \qquad \ldots (4)$$

the upper state should therefore correspond to the excitation of an electron from either a bonding $w\pi$ or $x\sigma$ orbital to the $v\pi$ antibonding orbital. For molecules with small internuclear distance, like NO⁺ and NS⁺ se may expect $x\sigma$ orbital to be higher in energy than $w\pi$. Thus the observed first excited ¹Π state arises from the configuration

$$\ldots (z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)(v\pi) \ldots {}^1\Pi \qquad \ldots (5)$$

However, for molecules with large internuclear distance like PO⁺, PS⁺ and AsO⁺ for which the ratios are observed to be almost equal, we would then expect the $x\sigma$ orbital to be lower in energy than the $w\pi$ orbital. Thus the first observed excited state in these molecules may be represented by the configuration

$$\ldots (z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^3(v\pi) \ldots {}^1\Sigma^+ \qquad \ldots (6)$$

Thus the singlet system of the AsO⁺ ion may be represented by the transition $A^1\Sigma - X^1\Sigma$. This assignment of the transition is supported by the observed simple rotational structure of the bands consisting of only R and P branches when photographed under the high dispersion of a E_1 quartz littrow spectrograph. (2 A/mm at λ2300 Å)

In his discussion of the electronic states of NO⁺, NS⁺, PO⁺ and PS⁺ Dressler (1955) has made the interesting observation that the vibrational frequencies of of the ground states of NO⁺ and PO⁺ agree closely with those of the excited states $A^2\Sigma$ and $A\ ^2\Sigma$ respectively of NO and PO as shown below

NO⁺ : $\omega''_e = 2377$ cm⁻¹   NO : $\omega'_e\ (A^2\Sigma) = 2375$ cm⁻¹

PO⁺ : $\omega''_e = 1405$ cm⁻¹   PO : $\omega'_e\ (A^2\Sigma) = 1391$ cm⁻¹

We have also observed that the vibrational frequency 1100 cm^{-1} of the ground state of AsO$^+$ agrees closely with the vibrational frequency 1098 cm^{-1} of the excited $B^2\Sigma$ state of AsO. Now, the $B^2\Sigma$ state of AsO was previously assigned to the configuration

$$\ldots (z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)^2 \ldots (\sigma) \ldots \; ^2\Sigma$$

in which the last electron is in a non-bonding orbital. If this electron is removed in the process of ionization of AsO molecule in the $B^2\Sigma$ excited state, we should expect no change in the vinrational frequency of the ground state of the ion thus formed. This plausible explanation of the near equality of the vibrational frequency of the B state with the ground state of the ion gives additional support to the assumption that the emitter of this singlet band system is the AsO$^+$ ion.

ACKNOWLEDGMENTS

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Letters to the Editor

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THE NEAR ULTRAVIOLET ABSORPTION SPECTRA OF THE THREE ISOMERIC METHYL PHENETOLES

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The near ultraviolet absorption spectra of ortho-, meta-, and para-methyl phenetoles were investigated in the vapour, liquid and solid phases.

Ortho-methyl phenetole :

In absorption in vapour about 20 bands were measured and the intense band at 2751.6 Å (36332 cm^{-1}) was taken as the (0, 0) band. The spectrum could be interpreted on the basis of four fundamental frequencies in the upper state (534, 734, 956 and 1275 cm^{-1}) and one fundamental in the ground state (428 cm^{-1}).

In absorption in solid state three bands were obtained and the intense band at 2787 Å (35870 cm^{-1}) was taken as the (0, 0) band. The spectrum could be interpreted on the basis of two upper state fundamentals (830 and 1952 cm^{-1}).

Meta-methyl phenetole.

In absorption spectrum of vapour about 23 bands were measured and the intense band at 2775.7 Å (36016 cm^{-1}) was taken as the (0, 0) band. The spectrum could be interpreted on the basis of five fundamental frequencies in the upper state (683, 741, 912, 1102 and 1279 cm^{-1}).

In absorption in liquid state three bands were obtained and the intense band at 2807 Å (35615 cm^{-1}) was taken as the (0,0) band. The spectrum could be interpreted on the basis of one upper state fundamental 897 cm^{-1}.

In absorption in solid state three bands were obtained and the intense band at 2805 Å (35640 cm^{-1}) was taken as the (0, 0) band. The spectrum could be interpreted on the basis of one upper state fundamental 886 cm^{-1}.

Para-methyl phenetole :

In absorption spectrum of the vapour about 35 bands were measured and the intense band at 2826.9 Å (35364 cm^{-1}) was taken as the (0, 0) band. The spectrum could be interpreted on the basis of six fundamental frequencies in the upper state (563, 635, 801, 989, 1120 and 1263 cm^{-1}) and one fundamental in the ground state (235 cm^{-1}).

In absorption in liquid state two bands were obtained and the intense band at 2873 Å (34797 cm^{-1}) was taken, as the (0, 0) band. The other band was interpreted as the upper state fundamental 830 cm^{-1}.

In absorption spectrum of the solid eleven bands were obtained and the intense band at 2880 Å (34712 cm^{-1}) was taken as the (0, 0) band. The spectrum was interpreted on the basis of three upper state fundamentals (452, 814 and 1197 cm^{-1}).

The details will be published shortly.

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STRUCTURE OF NAPHTHAZARIN, $C_{10}H_4O_2(CH)_2$

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Naphthazarin exists in three different modifications. The results of X-ray study on all these different forms have been summed up by Borgen (1956) and by Golder and Zhdanov (1958). A preliminary X-ray investigation on modification II, in the notations of Borgen, was made by Srivastava (1958) and later by Billy (1958) also. Billy has given the rough atomic positions which she estimated from three dimensional Patterson's synthesis and the projections obtained with the help of von Eller's photosummator.

In the present communication the molecular structure of naphthazarin has been determined by means of two-dimensional F_0-synthesis alsong [010]. The crystallographic data are :

$$a = 7.90 \text{ Å}, \quad b = 7.30 \text{ Å}, \quad c = 16.91 \text{ Å} \quad \text{and} \quad \beta = 124°38'$$

The crystal belongs to space group No. $14 P_{2_{1/c}} - C^5_{2h}$ and contains four molecules in a unit cell.

The molecular orientation was known from the study of magnetic anisotropies in the crystal by Banerji (1938). He further suggests that the intersections of the four molecular planes with (010) cannot all be along the same direction,

but should lie along two different directions in the (010) plane. This leads us to infer that the four molecules should exist in the unit cell, as two pairs, not related by any symmetry and that half-molecule should be taken as the asymmetric unit. This also supports the interpretation made by Billy on the basis of Patterson's function.

Accordingly, two molecules were placed in the unit cell with their centres at $0, 0, 0$ and $\frac{1}{2}, 0, 0$ which, after symmetry operations assigned to the space-group $P_{2_1/c}$, gave rise to two more molecules with their centres at $0, \frac{1}{2}, \frac{1}{2}$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, respectively. Atomic positions were found out from the electron density projection in the plane (010) and are given in the Table I. Molecules were well resolved in the plane (010) but much overlapping was found in (100) projection. Positions of the atoms in the projection (010) are shown in Fig. 1.
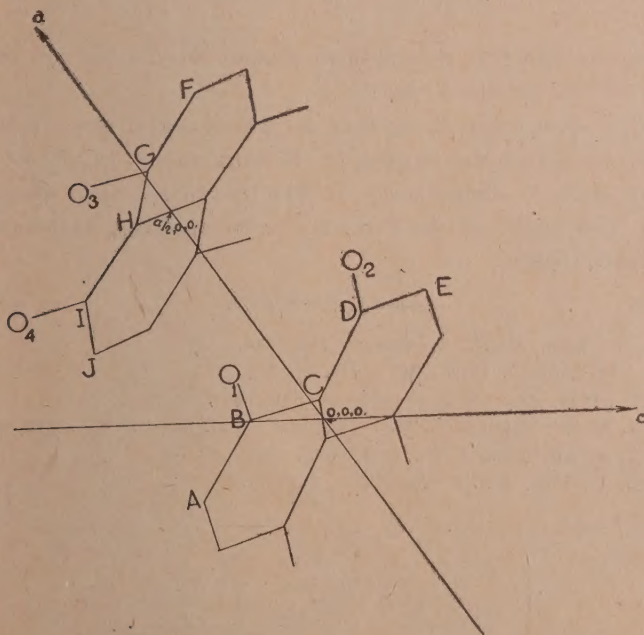
Fig. 1

In the calculation of the structure factors, Hoerni and Ibers' (1954) atomic form factors for oxygen and carbon have been used and an isotropic B-factor of 2.5×10^{-16} has been imposed upon them. The reliability index

$$R_{(hol)} = \frac{\Sigma \left| |F_0| - |F_c| \right|}{\Sigma |F_0|}$$

came out to be 0.23

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TABLE I

Molecule at 0,0,0			Molecule at $\frac{1}{2}$,0,0		
Atom	X_o in Å	Z_o in Å	Atom	Z_o in Å	Z_o in Å
A	−1.46	−2.57	F	6.04	1.62
B	0.00	−1.10	G	4.70	0.07
C	0.32	0.12	H	3.75	−0.61
D	1.98	1.72	I	2.35	−2.25
E	2.29	2.93	J	1.28	−2.76
O_1	0.71	−0.85	O_3	4.46	−0.90
O_2	2.67	2.00	O_4	2.02	−3.25

The complete structure of naphthazarin with Fourier and low temperature refinements will be published shortly.

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